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CHARLES DANZIGER SAMUELS

HISTORICAL INTRODUCTION

Numerous investigators have observed that many of the unfavorable physical and chemical properties of alkali soils are caused by a displacement of the normal soil bases. This displacement is brought about by the predominant bases of the soluble salts in the soil. In the treatment of alkali soils it is important, therefore, to bring about a reversal of this process to the end that the normal relationship of the replaceable bases may be ultimately restored. Various materials have been used for this purpose. Sulfur is of interest in this connection, since by its oxidation the necessary chemical changes may be brought about.

There are two sets of factors to be considered in the use of sulfur on alkali soils. First, the conditions influencing the oxidation, such as the effect of the soluble salts, varying alkaline reaction, aeration, etc. Second, the effect of the oxidation product, sulfuric acid, upon the soil. Previous studies on the oxidation of sulfur in alkali soils have been very limited and little is known concerning the influence of the concentration of sodium salts, alkalinity, etc., upon the speed of the reaction.

* Paper No. 157, University of California, Graduate School of Tropical Agriculture and Citrus Experiment Station, Riverside, California. Abridged from a thesis submitted to the University of California, November, 1925, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This investigation was supported by a Fellowship of the National Research Council, and was conducted under the direction of Dr. W. P. Kelley, to whom the writer is indebted for advice and criticism.

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Sulfur is mainly oxidized by biological action and the process is extracellular and autotrophic. *Thiobacillus thioparus* studied by Nathansohn,[21] Beijerinck, [1] and Jacobsen,[12] *Thiobacillus "B"* and *Thiobacillus thio-oxidans*, studied by J. G. Lipman and his associates,*[18] oxidize sulfur very readily and these organisms may be present in alkali soils.

The non-biological oxidation of sulfur has been studied by Kappen and Quensel,[13] Brown and Kellogg,[2] and MacIntyre, Gray, and Shaw.[19] The last named work was the most extended, in connection with which it was shown that non-biological oxidation of sulfur is not of great importance.

Hibbard[11] neutralized the alkalinity of soil by applying sulfur, and Rudolfs[22] reported that as a result of sulfur oxidation a desirable change takes place in the reaction and physical properties of alkali soils.

Kelley and Thomas[16] found that "sulfur undergoes reasonably active oxidation" in soils which contain large amounts of sodium salts. They found that the amount of sulfur necessary for the neutralization of the soil was equivalent to two or three times the soluble sodium carbonate. Since the work of Cummins and Kelley[4] and others shows that the exchange complex of alkaline soils may be sodium saturated, Kelley and Thomas believe that the excess of sulfur was used in double decomposition with the sodium complex of the soil.

The exchange properties of soils were first noted by Thompson[24] and then studied in detail by Way[26] who concluded that the active replacement material is a hydrated aluminum silicate. He later prepared silicates which exhibited the same type of base exchange. Eichhorn[6] and others[7, 17] have confirmed and amplified Way's results. Van Bemmelen[25] ascribed the exchange phenomena to the extended surface of the soil particles. Gans,[8] however, showed that the analogous base exchange property of artificial zeolites is chemical and that it depends upon their composition and structure and is independent of the size of the particles.

Gedroiz[10] concluded that with the exception of ammonia the replacing activity varies directly with the atomic weight and valence of the cation, and that the exchange capacity of a soil is a definite quantity. The exchange reaction was found to be reversible, and the equilibrium to be dependent upon relative masses and the atomic weight and valence of the salt. The reaction is instantaneous and is assumed to be a surface phenomenon.

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* For a very complete review of the sulfur oxidizing organisms see "Biochemical oxidation of sulfur and its significance to agriculture," by J. S. Joffe, New Jersey Agr. Expt. Sta. Bul. 374:1–91. 1922.

The Formation of Alkaline Soils.—The change produced by soluble salts on the composition of the reactive constituents of soils is of great significance in the formation of alkaline soils. The accumulated sodium salts, chiefly NaCl and Na_2SO_4, displace the calcium which predominates in productive soils[15] leaving sodium in its place. Upon leaching, either natural or artificial, the soil becomes alkaline. This alkalinity is considered by Gedroiz to be due to the hydrolysis of the sodium silicate complex. He concludes that calcium carbonate increases the soluble alkalinity according to the following reaction:

$$2\,NaX^* + CaCO_3 = CaX + Na_2CO_3.$$

Gedroiz[9] holds that the saline accumulations are the primary cause of soil alkalinity and the above equation suggests that the formation of sodium carbonate, through the action of calcium carbonate, is a step in the reclamation of the soil.

Dominicis'[5] theory is in agreement with that of Gedroiz' except as to the necessity of calcium carbonate for the formation of sodium carbonate. He states that the hydrolysis of the sodium complex results in the formation of sodium hydroxid which reacts with carbon dioxid to form sodium carbonate. Cummins and Kelley[4] have experimentally demonstrated the presence of sodium hydroxid when carbon dioxid was excluded from the system.

Relation between the Physical Characteristics and the Replaceable Bases.—The modification of a soil with a high content of replaceable calcium to a soil low in calcium and high in replaceable sodium results in profound changes in the physical properties of the soil. These changes were noted by Gans[8] in artificial zeolites and in soils receiving large applications of sodium nitrate. He also mentions the presence of a brown to black surface crust in these soils.

Sharp[23] has shown the increased colloidality produced in soils by treatment with salts (NaCl, Na_2SO_4, Na_2CO_3, and NaOH) by drying and weighing the material which remained in suspension in water. He clearly points out the relationship of the sodium replacement to the resulting deflocculated condition, which he ascribed to the sodium complexes thus formed.

A satisfactory chemical explanation of the potency of the divalent bases as flocculants and of the monovalent bases as deflocculants is not available. Among the more recent papers are those of Comber and Mattson. Mattson[20] ascribes the flocculating action of calcium hydroxid to the anomalous adsorption of negatively charged hydroxyl-

* This symbol is used throughout the paper to indicate the complex involved in replacement.

ions upon particles which are already negatively charged. This increase in the negative charges attracts the bivalent cation, calcium, which forms binding links and thus flocculates the particles. The monovalent ions possess no such linkage capacity.

Comber(3) differentiates between the colloidal nature of the core and the emulsoid surface of a clay particle. Calcium hydroxid is absorbed from dilute solutions only by the core of the particle and this process produces deflocculation. Absorption of calcium hydroxid in greater amounts results in its distribution on the emulsoid surface with the resulting flocculation of the particles.

EXPERIMENTAL METHODS AND RESULTS

Four different soils were used in these studies. Soil 5187 is an alluvial sand from the river-bottom lands west of Riverside, California. It is slightly alkaline and high in total soluble salts, and contains an abundance of calcium carbonate. Soil 5188 is a saline soil but not alkaline in reaction and contains practically no calcium carbonate. It is a fine sandy loam of the Fresno series and was obtained from an olive orchard on the Kearney Ranch, Fresno, California. Soil 5189 contains large amounts of sodium carbonate and is also a fine sandy loam of the Fresno series, similar in origin to soil 5188. The sample was taken from the worst portion of the University of California's Experimental Reclamation Tract on the Kearney Ranch, Fresno, California. It contains only small amounts of calcium carbonate. Soil 5190 is high in both soluble salts and calcium carbonate. It is a fine sandy loam of the Jordan series and was taken from the Terminal Sub Station Experimental Tract at Salt Lake City, Utah.*

Each of these samples was air dried, thoroughly mixed by screening and stored in large wooden bins. With the exception of soil 5188, which shows only slight effects of the salts upon olive trees growing in it, the areas from which the samples were taken were barren.

Sulfofication Experiments.—A set of sulfofication experiments was set up, using loosely covered two-quart Mason jars as containers. Sulfur was mixed with the soils in amounts varying from 0.15 to 2.00 per cent. The soils were kept near the optimum moisture content and samples were withdrawn for analysis at bi-weekly intervals.

* This sample was obtained through the kindness of Mr. R. A. Hart, Senior Drainage Engineer, United States Department of Agriculture, Salt Lake City, Utah.

The results expressed as parts per million of dry soil are reported in tables 1 and 2. These experiments, while primarily serving as an indication of the rate and extent of sulfur oxidation in these soils, have afforded further confirmation of the conclusions previously reached in this and other laboratories: namely, that sulfur readily undergoes oxidation in very alkaline soils and that this oxidation may ultimately result in the production of a neutral or acid reaction in the soil. The results from soils 5188 and 5189 offer an interesting contrast in that sulfofication was the more rapid in the soil which contained considerable sodium carbonate. It is also noteworthy that the alkaline soil contained much the higher total concentration of soluble salts.

TABLE 1

SULFOFICATION EXPERIMENTS WITH VARYING AMOUNTS OF SULFUR

Weeks	0.15 per cent S				0.25 per cent S				0.50 per cent S				1.00 per cent S			
	CO_3	HCO_3	SO_4	pH	CO_3	HCO_3	SO	pH	CO_3	HCO_3	SO_4	pH	CO_3	HCO_3	SO_4	pH
								Soil 5189								
0	1170	854	4354	9.8+	1170	854	4354	9.8+	1170	854	4354	9.8+	1170	854	4354	9.8+
2	1060	1170	4587	9.8+	1030	1090	4798	9.8+	1080	1070	4756	9.8+	1000	1130	4819	9.8+
4	980	810	4891	9.8+	960	910	5012	9.8+	880	960	5121	9.8+	890	1000	5364	9.8+
6	900	740	5186	9.8+	820	780	5301	9.8+	760	740	5505	9.8+	700	700	5739	9.8+
8	830	940	5414	9.8+	740	860	5779	9.8+	710	820	5919	9.8+	650	880	6204	9.8+
10	760	1010	5681	9.8+	710	1100	6143	9.8+	620	980	6387	9.8+	510	910	6616	9.8+
12	720	1230	5814	9.8+	680	980	6527	9.8+	550	1020	6843	9.8+	430	870	7120	9.8+
14	640	950	6020	9.8+	660	1070	6817	9.8+	470	1110	7184	9.8+	390	1080	7597	9.8+
16	510	810	6182	9.8+	530	1210	7084	9.8+	410	1190	7519	9.8+	360	1220	8064	9.8+
18	440	830	6307	9.8+	410	1140	7309	9.8+	430	1040	7921	9.8+	220	1160	8413	9.8+
20	320	1210	6451	9.8+	280	1320	7557	9.8+	190	1410	8347	9.4	111	1280	9012	9.0
22	270	930	6693	9.8+	160	1670	7721	9.6	104	1360	8562	9.4	58	1210	9306	8.6
24	260	1540	6814	9.8+	130	1980	7936	9.4	86	1310	8877	9.2	44	1130	9541	8.6
								Soil 5190								
0	211	409	3622	9.2	211	409	3622	9.2	211	409	3622	9.2	211	409	3622	9.2
2	150	370	4118	8.8	154	380	4148	8.8	140	342	4207	8.8	160	210	4251	8.8
4	136	312	4354	8.8	130	306	4519	8.8	108	288	4487	8.8	100	164	4560	8.8
6	110	288	4661	8.8	102	254	4711	8.6	90	210	4880	8.6	58	236	4767	8.6
8	64	240	5001	8.6	50	272	5107	8.4	42	254	5088	8.4	18	202	5212	8.4
10	22	270	5239	8.2	18	220	5340	8.2	10	276	5418	8.2	0	198	5671	8.2
12	10	224	5427	8.2	8	234	5561	8.2	0	214	5819	8.0	0	516	6033	7.8
14	0	306	5711	8.0	0	212	5841	8.0	0	480	6107	7.8	0	764	6354	7.8
16	0	418	5821	8.0	0	368	6012	7.8	0	615	6315	7.8	0	914	6580	7.8
18	0	560	6020	7.8	0	548	6241	7.8	0	976	6531	7.8	0	1130	6760	7.6
20	0	720	6345	7.8	0	872	6416	7.8	0	850	6844	7.6	0	1462	7003	7.4

TABLE 2

SULFOFICATION EXPERIMENTS WITH SOILS CONTAINING TWO PER CENT OF SULFUR

Soil 5189							Soil 5188						
Weeks	SO_4	CO_3	HCO_3	Ca	Mg	pH	Weeks	SO_4	CO_3	HCO_3	Ca	Mg	pH
0	4354	1170	854	0	0	9.8+	0	1437	0	156	68	18	7.4
2	4601	950	1060	0	0	9.8	2	1671	0	305	134	31	7.4
4	5004	980	810	0	0	9.8	4	1901	0	196	226	40	7.4
6	5224	1120	870	0	0	9.8	6	2354	0	88	402	64	7.2
8	5571	780	1210	0	0	9.8	8	2418	0	34	467	60	7.2
10	5824	430	1450	0	0	9.8	10	2461	0	40	480	72	7.2
12	6212	370	1780	0	0	9.8	12	2512	0	54	482	63	7.2
14	6784	230	1990	0	0	9.8	14	2498	0	28	511	68	7.0
16	7627	140	2200	0	0	9.8	16	2524	0	20	501	51	6.8
18	8523	72	1410	0	0	9.2	18	2560	0	32	520	72	6.8
20	9419	32	1090*	18	0	8.4	20	2540	0	18	524	68	6.8
22	10287	0	1010*	309	41	8.0	22	2585	0	18	555	70	6.8
24	10940	0	940*	518	68	7.6	24	2611	0	24	573	72	6.8
26	11817	0	809*	842	77	7.2							
28	13004	0	602*	1350	91	6.8							
30	15217	0	204	2012	111	6.8							
Soil 5190							Soil 5187						
Weeks	SO_4	CO_3	HCO_3	Ca	Mg	pH	Weeks	SO_4	CO_3	HCO_3	Ca	Mg	pH
0	3622	211	409	18	[illegible]	9.2	0	2535	144	256	8	0	8.2
2	4418	140	312	12	0	8.8	[illegible]	6518	0	306	1214	101	7.4
4	4612	124	210	22	0	8.8	4	14702	0	184	4421	178	7.0
6	4900	106	374	16	0	8.8							
8	5166	52	291	34	0	8.4							
10	5318	22	220	47	10	8.2							
12	5677	0	510	218	21	7.8							
14	6019	0	884	410	47	7.8							
16	6771	0	1214	656	52	7.6							
18	6944	0	1320	784	70	7.2							
20	7520	0	1200	1012	91	6.8							

* The extract gradually changed in color from a dark brown through a straw color to colorless in these samples.

The data show that as oxidation continued the content of sulfate increased while soluble carbonate decreased and the bicarbonate fluctuated considerably. This fluctuation in bicarbonate is quite striking in all the soils studied. In certain cases there was a distinct decrease in bicarbonate in the presence of normal carbonate. Since dilute acids convert carbonate into an equivalent amount of bicarbonate, the sum of these salts should be constant as long as the normal carbonate remains in solution. From the graph (fig. 1) plotted for one of these soils it is apparent that such a reciprocal relationship between carbonate and bicarbonate was not maintained

under these conditions. The lack of correlation between carbonate decomposition and bicarbonate formation occurred in varying degrees in all the soils studied.

Upon the neutralization of all of the soluble carbonate there was an immediate increase in the amount of soluble calcium, a result which is to be expected from the solubility of the calcium salts and is mentioned at this point because of the important relationship it bears to the use of sulfur, as brought out in later studies.

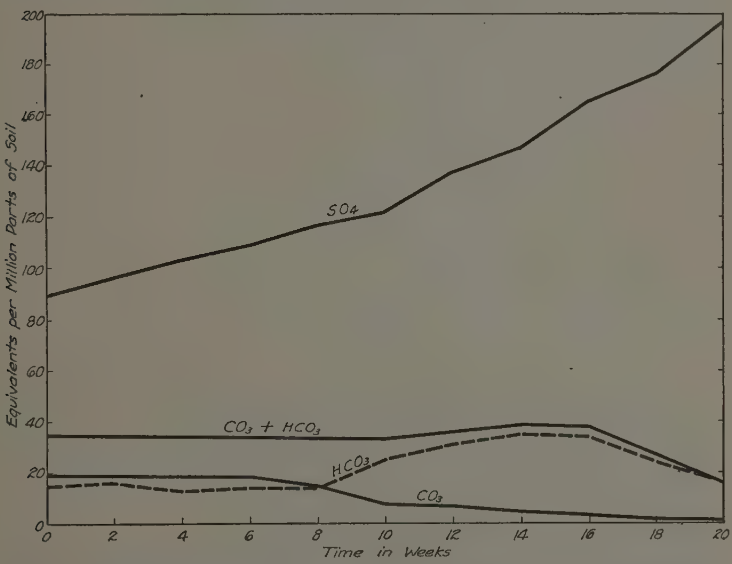

Fig. 1. The relation between the formation of sulfate and the decomposition of carbonate and bicarbonate in sulfofication experiments with soil 5189.

These experiments indicate clearly that there is no apparent relationship between the number of equivalents of sulfate formed and the number of equivalents of carbonate neutralized. The data from one series of analyses, shown graphically in figure 1, makes it evident that much more sulfate was formed than was necessary to account for the carbonate neutralized. In fact, an excess of sulfate was formed above the amount necessary to account for both the carbonate and the bicarbonate neutralized. This lack of close relationship between sulfate formation and the neutralization of carbonate and bicarbonate, as well as the simultaneous decomposition of both carbonates and bicarbonates, was clearly pointed out by Kelley and Thomas.[16]

These results and those of other workers, as well as the data obtained in field trials to be discussed later, indicate that sulfur will undergo relatively active oxidation in alkali soils. However, the anomalous decomposition of bicarbonate in the presence of normal carbonate and the inability to obtain even approximate correlations between sulfate formation and carbonate decomposition in the carefully controlled laboratory experiments seemed rather puzzling. Further experiments were accordingly made in an attempt to find a rational explanation of the chemical changes occurring within the soil. Since sulfur becomes oxidized to sulfuric acid and the chemical changes are due to the action of this acid, a study was made of the effects produced by the addition of solutions of sulfuric acid.

Alkaline Soils and Sulfuric Acid.—Dilute solutions of sulfuric acid were shaken with the soil in the ratio of 5 to 1. The shaking was continued for two hours, when the solutions were filtered through Pasteur-Chamberland filters. The first 250 cc. of filtrate was discarded and the remainder was analyzed by standard methods[14] for CO_3, HCO_3, Cl, SO_4, SiO_2, Na, K, Ca, and Mg. The accuracy of the bicarbonate titration is limited by the color change of methyl orange, which is not very distinct in the dark-colored soil extracts common to alkaline soils. The carbonate titration with phenolphthalein, however, is accurate despite the dark color, since the color change is pronounced. By calculating the difference between the total CO_2 and the CO_2-equivalent of the normal carbonate, an accurate bicarbonate determination was made possible. The total CO_2 was determined in 100 cc. of the extract by adding 50 cc. of 0.15N HCl and absorbing the evolved CO_2 in 0.10 N KOH. The KOH was then titrated to the phenolphthalein end point and the CO_2 contained in the standard alkali subtracted from the total CO_2 figure thus obtained. Duplicate determinations checked within 0.1 cc. of 0.10 N KOH.

TABLE 3

COMPOSITION OF DILUTE H_2SO_4 EXTRACTS OF SOIL 5189

Parts per million of dry soil

Treatment	CO_3	HCO_3	CO_2	Cl	SO	SiO_2	Ca	Mg
H_2O	1105	1160	1635	8233	4257	76	42	20
0.0034 N H_2SO_4	650	1479	1625	8261	4989	74	74	20
0.0040 N H_2SO_4	480	1653	1645	8237	5200	57	82	22
0.0050 N H_2SO_4	288	2083	1630	8275	5351	49	102	18
0.0057 N H_2SO_4	267	2031	1620	8252	5445	64	142	21
0.0066 N H_2SO_4	120	2316	1625	8257	5687	75	151	20
0.0070 N H_2SO_4	Trace	2435	1640	8264	5831	64	192	21
0.0075 N H_2SO_4	0	2468	1645	8271	6052	68	254	28
0.0080 N H_2SO_4	0	2513	1630	8252	6152	67	258	44

TABLE 4

COMPOSITION OF DILUTE H_2SO_4 EXTRACTS OF SOIL 5189 AFTER LEACHING WITH WATER

Parts per million of dry soil

Treatment	CO_3	HCO_3	CO_2	Cl	SO_4	SiO_2	Ca	Mg	Na	K
H_2O	59	752	610	10	45	56	0	12	310	18
0.0005 N H_2SO_4	26	733	605	10	154	62	0	11	342	44
0.0010 N H_2SO_4	9	740	635	12	263	55	0	10	381	56
0.0015 N H_2SO_4	0	729	625	10	421	55	23	9	402	78
0.0020 N H_2SO_4	0	800	615	12	531	54	66	9	414	91
0.0025 N H_2SO_4	0	843	635	10	652	57	95	10	426	103

TABLE 5

COMPOSITION OF DILUTE SULFURIC ACID EXTRACTS OF SOIL 1869

Parts per million of dry soil

Treatment	CO_3	HCO_3	CO_2	Cl	SO_4	SiO_2	Ca	Mg	Na	K
H_2O	141	589	570	52	47	43	24	12	307	48
0.0005 N H_2SO_4	99	613	555	50	162	47	26	12	335	68
0.0010 N H_2SO_4	48	741	550	50	281	46	25	12	371	81
0.0015 N H_2SO_4	0	851	590	48	369	50	27	11	407	90
0.0020 N H_2SO_4	0	833	575	49	486	47	52	12	425	94
0.0025 N H_2SO_4	0	827	575	48	583	46	75	14	451	100

TABLE 6

COMPOSITION OF DILUTE SULFURIC ACID EXTRACTS OF SOIL 5696

Parts per million of dry soil

Treatment	CO_3	HCO_3	CO_2	Cl	SO_4	SiO_2	Ca	Mg	Na	K
H_2O	336	497	395	4827	1774	97	28	16	4097	20
0.0005 N H_2SO_4	312	479	385	4834	1915	88	28	13	4160	31
0.0010 N H_2SO_4	273	625	385	4823	2077	87	28	12	4195	49
0.0015 N H_2SO_4	258	653	390	4889	2217	74	30	12	4271	68
0.0020 N H_2SO_4	204	708	410	4856	2276	69	31	14	4337	77
0.0025 N H_2SO_4	180	805	440	4879	2330	69	35	13	4376	91
0.0030 N H_2SO_4	189	817	470	4828	2381	66	42	18	4307	86
0.0035 N H_2SO_4	144	1079	595	4831	2496	62	46	17	4399	100
0.0040 N H_2SO_4	135	1135	610	4885	2646	63	47	21	4425	121
0.0045 N H_2SO_4	123	1186	660	4920	2729	64	49	22	4583	138
0.0050 N H_2SO_4	123	1226	690	4855	2354	61	56	27	4646	144
0.0055 N H_2SO_4	102	1369	850	4831	2983	60	68	31	4700	169
0.0080 N H_2SO_4	Trace	1781	1020	4838	3726	90	132	37	5284	188
0.0150 N H_2SO_4	0	2925	1860	4811	5456	128	321	56	6187	224
0.0250 N H_2SO_4	0	3577	2300	4873	7116	157	779	68	6531	287

TABLE 7

COMPOSITION OF DILUTE SULFURIC ACID EXTRACTS OF SOIL 5190

Parts per million of dry soil

Treatment	CO_3	HCO_3	CO_2	Cl	SO_4	SiO_2	Ca	Mg	Na	K
H_2O	162	991	810	61	54	45	16	15	530	32
0.0005 N H_2SO_4	120	1095	805	63	167	64	19	13	560	44
0.0010 N H_2SO_4	120	1020	800	56	286	73	19	13	620	56
0.0015 N H_2SO_4	71	1275	825	55	407	51	24	16	660	61
0.0020 N H_2SO_4	58	1354	900	54	528	45	25	20	691	80
0.0025 N H_2SO_4	53	1394	925	57	657	43	30	23	744	87
0.0030 N H_2SO_4	44	1450	955	61	775	43	34	27	971	90
0.0035 N H_2SO_4	38	1566	1045	57	873	45	57	40	848	98
0.0040 N H_2SO_4	33	1670	1130	55	972	46	83	44	899	100
0.0045 N H_2SO_4	21	1724	1220	57	1036	51	89	57	931	101
0.0050 N H_2SO_4	10	1800	1295	60	1196	53	100	70	1013	99
0.0055 N H_2SO_4	Trace	1841	1360	70	1297	49	102	74	1057	103
0.0060 N H_2SO_4	Trace	1880	1460	68	1429	54	135	83	1110	106
0.0065 N H_2SO_4	Trace	1991	1540	64	1551	64	142	96	1176	104
0.0070 N H_2SO_4	Trace	2036	1605	66	1681	69	170	104	1238	100

The data in tables 3, 4, 5, 6, and 7 were obtained from soils 5189, 5190, 5696 (a Lahontan clay from Fallon, Nevada), and 1869 (a Fresno fine sandy loam from Kearney Ranch, Fresno, California). Soils 5189 and 5190 were leached to remove the excess of soluble sodium salts, which interfere with an accurate determination of sodium.

Under these conditions the effect of sulfuric acid was very different from that which takes place in a soil during sulfur oxidation. The addition of sulfuric acid always resulted in a decrease in normal carbonate and an approximately equivalent increase in bicarbonate. In every soil to which increasing amounts of sulfuric acid were added, the following regular changes were noted up to the point where soluble normal carbonate disappeared: (*1*) A decrease in normal carbonate and a reciprocal increase in bicarbonate; (*2*) an increase in sulfate equivalent to that added as H_2SO_4; (*3*) an increase in soluble sodium and potassium with every increase in the concentration of sulfuric acid; (*4*) not more than a slight increase in calcium and magnesium until the normal carbonate was greatly reduced, but with the neutralization of all of the normal carbonate there was an immediate increase in soluble calcium and magnesium; (5) only slight changes in soluble SiO_2.

In order to show the possible reactions produced by the acid, the data in the above tables have been recalculated on the basis of the following assumptions:

First, that the decrease in carbonate is accounted for by the equation: $2\,Na_2CO_3 + H_2SO_4 = Na_2SO_4 + 2\,NaHCO_3$.

Second, that the increase in soluble sodium and potassium is accounted for by one or more of the following type equations:

(*1*) $2\,NaX + H_2SO_4 = 2\,HX + Na_2SO_4$

(*2*) $2\,CaCO_3 + H_2SO_4 = CaSO_4 + Ca(HCO_3)_2$

$4\,NaX + CaSO_4 + Ca(HCO_3)_2 = 2\,CaX_2 + Na_2SO_4 + 2\,NaHCO_3$.

Third, that any increase in calcium and magnesium was due either to the solubility of $CaCO_3$, $MgCO_3$ or silicates in the saline solution, or to the following reaction:

$$CaX_2 + H_2SO_4 = 2\,HX + CaSO_4.$$

The foregoing data calculated on the basis of these assumptions are shown in tables 8, 9, 10, and 11.

TABLE 8

THE EFFECT OF SULFURIC ACID ON SOIL 5189, CALCULATED FROM THE DATA OF TABLE 4

Expressed as equivalents per million parts of soil

(1)	(2)	(3)	(4)	(5)	(6)	(7)
	Replaced					
Na_2CO_3 neutralized	Na	K	Total of (1), (2), and (3)	H_2SO_4 added	Difference between (4) and (5)	Calcium brought into solution
0.55	1.40	0.65	2.60	2.50	+0.10	0.00
0.83	3.10	1.00	4.93	5.00	−0.07	0.00
1.00	4.00	1.50	7.65	7.50	+0.15	1.15
1.00	4.52	1.82	10.64	10.00	+0.64	3.30
1.00	5.00	2.17	12.92	12.50	+0.42	4.75

TABLE 9

THE EFFECT OF H_2SO_4 ON SOIL 1869, CALCULATED FROM THE DATA OF TABLE 5

Expressed as equivalents per million parts of soil

(1)	(2)	(3)	(4)	(5)	(6)	(7)
	Replaced					
Na_2CO_3 neutralized	Na	K	Total of (1), (2), and (3)	H_2SO_4 added	Difference between (4) and (5)	Calcium brought into solution
0.70	1.22	0.50	2.42	2.50	−0.08	0.00
1.55	2.78	0.80	5.13	5.00	+0.13	0.00
2.35	4.35	1.05	7.75	7.50	+0.25	0.00
2.35	5.13	1.15	10.03	10.00	+0.03	1.40
2.35	6.26	1.30	12.46	12.50	−0.04	2.55

TABLE 10

THE EFFECT OF H_2SO_4 ON SOIL 5696, CALCULATED FROM THE DATA OF TABLE 6

Expressed as equivalents per million parts of soil

(1)	(2)	(3)	(4)	(5)	(6)	(7)
	Replaced					
Na_2CO_3 neutralized	Na	K	Total of (1), (2), and (3)	H_2SO_4 added	Difference between (4) and (5)	Amount of calcium brought into solution which in turn replaced Na
0.40	2.74	0.27	3.41	2.50	+0.91	0.0
1.05	4.26	0.62	5.93	5.00	+0.93	0.0
1.30	7.58	1.20	10.08	7.50	+2.58	0.0
2.20	10.43	1.42	14.05	10.00	+4.05	0.0
2.51	12.10	1.78	16.39	12.50	+3.89	0.8
2.45	9.13	1.65	13.23	15.00	−1.77	1.3
3.27	13.13	2.00	18.40	17.50	+0.90	4.0
3.35	14.26	2.50	20.11	20.00	+0.11	4.1
3.55	21.10	2.95	27.60	22.50	+5.10	5.2
3.55	23.95	3.10	30.60	25.00	+5.60	5.5
3.90	26.20	3.72	33.82	27.50	+6.32	9.7
5.60	51.50	4.20	61.30	40.00	+21.30	10.7
5.60	90.90	5.10	101.60	75.00	+26.60	24.3
5.60	106.00	6.60	118.20	125.00	−6.80	22.4

TABLE 11

THE EFFECT OF H_2SO_4 ON SOIL 5190, CALCULATED FROM THE DATA OF TABLE 7

Expressed as equivalents per million parts of soil

(1)	(2)	(3)	(4)	(5)	(6)	(7)
	Replaced					
Na_2CO_3 neutralized	Na	K	Total of (1), (2), and (3)	H_2SO_4 added	Difference between (4) and (5)	Amount of calcium brought into solution which in turn replaced Na
0.70	1.30	0.30	2.30	2.50	−0.20	0.0
0.70	3.90	0.60	5.20	5.00	+0.20	0.0
1.50	5.60	0.70	7.80	7.50	+0.30	0.0
1.73	7.00	1.20	9.93	10.00	−0.07	1.7
1.81	9.30	1.40	12.51	12.50	+0.01	1.6
1.97	11.40	1.50	14.87	15.00	−0.03	2.3
2.07	13.90	1.70	17.67	17.50	+0.17	3.3
2.15	16.00	1.70	19.85	20.00	−0.15	4.5
2.35	18.40	1.80	22.55	22.50	+0.05	6.0
2.54	20.70	1.70	24.94	25.00	−0.06	6.6
2.70	22.90	1.80	27.40	27.50	−0.10	7.8
2.70	25.20	1.80	29.70	30.00	−0.30	9.0
2.70	28.10	1.80	32.60	32.50	+0.10	10.1
2.70	30.70	1.70	35.10	35.00	+0.10	10.4

By means of these assumptions, which are based upon our present theories concerning the origin and properties of alkaline soils, it is possible, with one exception, to account almost quantitatively for all of the sulfuric acid that was added to these soils. The recalculation of the data in this way makes possible a much clearer picture of the possible reactions between the acid and the alkaline materials of the

soil. Thus in accounting for the 2.50 equivalents of acid added to soil 5190 it is seen that 0.70 equivalents reacted with sodium carbonate, 1.30 equivalents was exchanged for sodium and 0.30 equivalents was exchanged for potassium.

Upon approaching the complete neutralization of Na_2CO_3 in soil 5696, the increase in soluble sodium was greatly in excess of the theoretical amount. This soil differs from the other soils studied in that it contains a high concentration of soluble salts. It is also high in calcium carbonate. The salinity greatly complicates the analytical determination of sodium and potassium, a fact which may in part account for the results obtained. The extreme divergence upon the approach of complete neutralization of all of the normal carbonate is, however, greatly in excess of any possible analytical error.

It is known that neutral sodium salts increase the solubility of $CaCO_3$. The gradually increasing amounts of calcium found as the neutralization of carbonate proceeded was probably due in part at least to this type of solution. Moreover, if it is assumed that the sulfuric acid reacts with calcium carbonate as represented by the equation $2\,CaCO_3 + H_2SO_4 = Ca(HCO_3)_2 + CaSO_4$, it is apparent that one equivalent of acid may bring two equivalents of calcium into solution. This calcium may then be exchanged for sodium and thus result in the bringing of two equivalents of sodium into solution for one equivalent of acid. Accordingly any attempt to account quantitatively for the sulfuric acid added under these conditions is considerably complicated.

The Partition of the Added Acid.—The data show that the amount of acid necessary to effect the neutralization of an alkali soil may be much greater than the theoretical figure that is indicated by the amount of soluble carbonate present. Two changes were noted with the first increments of acid added. Each increment decreased the concentration of sodium carbonate and increased the concentration of soluble sodium. The reaction may be considered as an immediate reaction between sodium carbonate and sulfuric acid followed by a further hydrolysis, or it may be considered as a partitioning of the acid as illustrated by the following:

$$\begin{aligned} 2\,Na_2CO_3 + H_2SO_4 &= 2\,NaHCO_3 + Na_2SO_4 \\ NaX + H_2O &= NaOH + HX \\ 2\,NaOH + H_2SO_4 &= Na_2SO_4 + 2\,H_2O \end{aligned}$$

or

$$\begin{matrix} NaX \\ \\ Na_2CO_3 \end{matrix} + H_2SO_4 = \begin{matrix} Na_2SO_4 \\ \\ NaHCO_3 \end{matrix} + HX$$

The equilibrium is the same in either case and it is of slight significance which reaction is favored. A partitioning of the acid, that is, an immediate neutralization of both the alkaline silicate complexes and the sodium carbonate more clearly emphasizes the degree of alkalinity of the two compounds. The greater portion of the sulfuric acid will react with the more alkaline compound, in this case the alkaline silicate complex. The active neutralization of the acid by the silicate complex is in a measure a verification of the potential presence of NaOH in the soil, as was experimentally shown by Cummins and Kelley.[4]

The following data show the amount of acid required to neutralize the soluble sodium carbonate in a 1–5 water extract of the soil, and the total amount of acid which it was necessary to add to the soil in order to neutralize both the alkaline silicates and the sodium carbonate.

TABLE 12

DATA SHOWING THE RELATION BETWEEN SODIUM CARBONATE AND TOTAL ALKALINITY OF SOILS

	Equivalents of acid required to neutralize	
	Na_2CO_3	Total alkalinity
Soil 5190 (leached)	2.70	35.00
Soil 5696 (unleached)	5.60	40.00
Soil 5189 (leached)	1.00	7.50
Soil 5189 (unleached)	18.50	35.00
Soil 1869 (leached)	2.35	7.50

The data of table 12 show that the amount of sodium carbonate present is no necessary indication of the amount of acid required to neutralize all of the alkalinity of the soil. Although the reactions which take place in alkali soils as sulfur is oxidized differ somewhat from those produced by a solution of sulfuric acid, it seems certain that the amount of sulfur required in the practical treatment of an alkali soil may greatly exceed the sulfur equivalent of its soluble carbonate and bicarbonate content. In the case of soil 5189, it is also shown that the leaching with water greatly reduced both the soluble and the total alkalinity. The latter was reduced by leaching alone from 35 to 7.5 equivalents of acid. The advisability of such leaching in the reclamation af an alkaline soil is, however, very doubtful, since a large part of the organic matter and the colloidal material will be washed down along with the salts, and the remaining soil may then be mainly a sand unsuited to the growth of crops. There is also an unnecessarily large loss of plant nutrients, as emphasized by Hilgard and others.

Rôle of Hydrogen Ions in the Neutralization of Soil Alkalinity.—In considering alkaline soils it has been found desirable to separate them into two classes; namely those high in calcium carbonate and those low in calcium carbonate. The exact amounts which determine this classification have not been considered in the present paper. The samples obtained from the Kearney Ranch, soils 1869 and 5189, are low in calcium carbonate. The addition of acid to these soils up to the point of converting all of the sodium carbonate into sodium bicarbonate yielded no increase in total CO_2 in the extract. From this result it is concluded that calcium carbonate was not involved in the reaction. Furthermore, since no significant change was noted in the concentration of the soluble parts other than Na and K, it must be assumed that the only replacing agent was the H ion. Such a statement does not imply, however, that the complete neutralization of an alkaline soil would result in a soil saturated mainly with H ions.

It was also found that the increase in calcium brought into solution in these two soils upon neutralization of all of the sodium carbonate was not accompanied by an increase in CO_2. Therefore, the conclusion is drawn that the source of this dissolved calcium was mainly silicates. This further emphasizes the importance of calcium carbonate in the application of sulfur or sulfuric acid to an alkaline soil, for in the absence of $CaCO_3$, H ions not only replace sodium from the silicate complex, but may also bring calcium into solution from the limited supply of calcium silicate present. The sulfuric acid will thus further impoverish the soil of its calcium. This conclusion is in harmony with Gedroiz' findings upon the energy of absorption of H ions as previously mentioned.

In the presence of calcium carbonate the equilibrium conditions are very different. The first few additions of acid yielded results similar to those found in the absence of calcium carbonate. With further additions there was an increase in the total CO_2 extracted and an increase in soluble calcium. The increase in soluble calcium took place in the presence of soluble carbonate and is due to the greater solubility of $CaCO_3$ in the increasingly saline solution. However, the increase in CO_2 was much greater than the increase in soluble calcium. The difference between the calcium carbonate dissolved and the CO_2 found is assumed to represent the amount of calcium which was first brought into solution from calcium carbonate but which then served to replace sodium* from the silicate complex and thus passed out of

* Throughout this discussion the terms "sodium and "calcium" are used without mention of potassium and magnesium, which are similarly involved in all of these changes to a lesser extent. It is not intended to imply their absence in the reactions, but these words are simply so used to avoid the mention of both monovalent or divalent salts each time they are considered.

solution. The data showing the approximate extent of this replacement are given in tables 10 and 11. The accuracy of these calculations is limited by the uncertainty as to what extent magnesium acted as a replacing agent. However, the error is of no significance in the present case, since the intent is simply to indicate the relative extent to which hydrogen ions and calcium acted as replacing agents in these soils. If the results are subtracted from the total calcium and magnesium as shown in tables 6 and 7, it is possible to gain an approximate idea of the extent to which hydrogen and calcium have displaced sodium.

These results indicate that even in the presence of large amounts of calcium carbonate the replacement of Na was effected mainly by H ions. Upon the complete neutralization of the sodium carbonate the proportion of hydrogen ions which served to replace sodium decreased, and the amount of calcium which acted as a replacing agent for sodium increased. The exact amounts of replacement brought about by calcium and hydrogen ions after all of the sodium carbonate was neutralized cannot be determined with accuracy, since a small loss of carbon dioxide took place. Since the calcium in solution rapidly increased, it seems probable that it would ultimately predominate as a replacing agent.

No extended study was made on the physical state of the soils as affected by these treatments. Several series of cylinder experiments on the rate of settling of the sulfuric-acid-treated soils indicate that upon the replacement of sodium there was a marked flocculation of the soil particles. The rate of settling of the soils before filtration was always more rapid and more complete where the larger amounts of acid were used. Rudolfs[22] reported similar results in soils in which sulfur oxidation had taken place. Whether the flocculating action was due to H ions cannot be stated, since with sufficient replacement of Na by H ions to observe this change, there was always an increase in calcium in the solution. The flocculating action of Ca, as already stated, is very great.

Alkaline Soils and Calcium Sulfate.—It has already been pointed out that upon the addition of sulfuric acid to alkaline soils the equilibrium is not the same as that resulting from sulfur oxidation. The effect of calcium sulfate seems to offer, in part, an explanation for this difference.

The same procedure was followed in these studies as with the sulfuric acid. A saturated solution of calcium sulfate was prepared and diluted to known concentrations and added to the soil. The results are reported in tables 13 and 14.

TABLE 13

DATA SHOWING THE DIFFERENCE PRODUCED IN SOIL 5190 BY ADDING EQUIVALENT AMOUNTS OF $CaSO_4$ AND H_2SO_4

Parts per million

Treatment	CO_3	HCO_3	CO_2	Cl	SO_4	SiO_2	Ca	Mg	Na	K
H_2O	162	991	810	61	54	45	16	15	530	32
0.0025 N H_2SO_4	53	1344	900	57	657	43	30	23	731	87
0.0025 N $CaSO_4$	150	682	600	58	621	47	27	41	552	42
0.0050 N H_2SO_4	10	1614	1295	60	1196	53	120	80	893	99
0.0050 N $CaSO_4$	132	510	505	55	1141	61	66	68	634	51
0.0070 N H_2SO_4	Trace	1978	1605	66	1681	69	270	144	968	100
0.0070 N $CaSO_4$	80	344	450	61	1659	54	136	86	708	42

TABLE 14

DATA SHOWING THE DIFFERENCE PRODUCED IN SOIL 5696 BY ADDING EQUIVALENT AMOUNTS OF $CaSO_4$ AND H_2SO_4

Parts per million

Treatment	CO_3	HCO_3	CO_2	Cl	SO_4	SiO_2	Ca	Mg	Na	K
H_2O	336	497	395	4827	1724	97	28	16	4097	20
0.0025 N H_2SO_4	180	805	440	4879	2330	69	35	13	4376	91
0.0025 N $CaSO_4$	356	189	180	4832	2178	80	46	30	4104	84
0.0050 N H_2SO_4	123	1226	690	4855	2854	61	56	27	4646	144
0.0050 N $CaSO_4$	326	207	145	4888	2749	62	72	35	4347	121
0.0150 N H_2SO_4	0	2925	1860	4811	5456	128	321	56	6187	224
0.0150 N $CaSO_4$	310	85	100	4907	5291	61	160	39	5382	194

A large part of the added $CaSO_4$ was precipitated as $CaCO_3$. The remainder replaced sodium from the silicate complex. The precipitation of $CaCO_3$ was evident from the marked decrease in the concentration of CO_2 in the extract. Upon precipitation of calcium carbonate the corbonate-bicarbonate equilibrium of the soil was disturbed, and in the presence of alkaline silicate complexes and the products of their hydrolysis a portion of the bicarbonate was converted into carbonate. Thus the precipitation of normal carbonate reduced the concentration of bicarbonates, owing to the alkalinity of the silicate complexes. That these silicate complexes are a primary source of alkalinity is evident, since the concentration of sodium carbonate was only slightly decreased by large additions of calcium sulfate.

The data show that calcium sulfate is not nearly as effective as sulfuric acid in the replacement of sodium from the silicate complex. This is due to differences in the type of reaction. Calcium sulfate

functions, in considerable part, to precipitate the carbonate as calcium carbonate with the simultaneous formation of sodium sulfate. Sulfuric acid, on the other hand, only partially neutralizes the sodium carbonate by forming the bicarbonate. Consequently a given amount of sulfuric acid removed a greater amount of the normal carbonate than did an equivalent amount of calcium sulfate.

Absorption of Carbon Dioxide by Soil Organisms.—If it is assumed that the process of sulfur oxidation in alkaline soils is in part a localized reaction around particles of calcium carbonate, it is possible to explain the apparently anomalous carbonate-bicarbonate results of the sulfur-oxidation experiments. The organisms are autotrophic and by means of a localized activity around $CaCO_3$ particles they may obtain the carbon necessary for their growth, and in the presence of calcium carbonate the end product of the reaction, sulfuric acid, is neutralized. The calcium sulfate formed during this reaction, upon diffusion from these localized zones, would in turn be again precipitated as calcium carbonate. This reaction would affect the carbonate-bicarbonate equilibrium to the extent to which CO_2 was lost from the system, somewhat as was the case when $CaSO_4$ was added.

Under the conditions that exist in the soil during sulfur oxidation, a decrease in bicarbonate involves either the changes hypothecated or a loss of carbon dioxide to the air. Since the results presented were obtained in soils containing sodium carbonate, the loss of carbon dioxide to the air should have been very small. Whether calcium carbonate plays such a rôle in sulfur oxidation or not, its presence in large amounts in an alkaline soil may be regarded as potentially valuable in their reclamation by means of sulfur, since it affords a source of calcium which the products of sulfur oxidation may bring into solution and thus make available as a plant nutrient, besides effecting the substitution of sodium in the exchange complex.

Tank Experiments.—Galvanized iron containers 19 inches in diameter and 24 inches in height were used in these experiments. Two hundred and fifty pounds of soil was added to each container, and placed upon a layer of broken granite to permit drainage through an opening in the bottom. Soils 5189 and 5190 were used. Six cans of each soil were set up, and each of the following treatments was applied to one can of each set: 100 grams sulfur after the soil was thoroughly leached; 100 grams sulfur without previous leaching; 100 grams sulfur and 85 grams calcium carbonate; 100 grams sulfur and 116 grams calcium sulfate; sulfuric acid equivalent to 100 grams sulfur applied as 0.05 N solution. The amounts of the several

treatments correspond to those used in the field experiments referred to later. The materials were thoroughly mixed with the surface 6 inches of soil on March 15, 1924, and allowed to stand with occasional irrigations and cultivations. Samples were drawn from the first foot and the second foot on May 10, 1924, and October 10, 1924. The soils were leached with water on November 26, 1924, and again sampled on January 2, 1925. Barley was planted on January 2, 1925, and the crop harvested May 6, 1925. The final sampling was made on June 12, 1925, after a very slight leaching made for the purpose of washing the products of sulfur oxidation down into the lower layers of the soil.

Practically all of the sodium carbonate was neutralized within fifteen months' time in the soils of every treated tank. With the rather large accumulations of soluble calcium in the second foot of the soil, it seems apparent that the neutralization must have taken place at the expense of a portion of the surface calcium, which was washed down in the leaching process. This loss of calcium was the more apparent in soil 5190, which is high in calcium carbonate. The same fluctuation in the bicarbonate and its decomposition took place in these tank experiments as in the sulfur-oxidation experiments.

Barley was planted in each of the soils on January 2, 1925. The seeds germinated in each of the twelve tanks, but at the end of two weeks the plants in the check tanks began drying up at the tips of the leaves and soon died. In the tanks receiving sulfur alone before and after leaching, the plants attained a height of about 6 inches and then died back from the tips of the leaves as did the check plants. In none of the tanks was a satisfactory growth obtained.

The best growth of the barley as judged by its appearance and final yield was on the Utah soil to which were added sulfur and calcium carbonate, and sulfur and calcium sulfate. This seemed rather surprising in view of the large amounts of calcium carbonate initially present in this soil. The best growth on the Fresno soil was where sulfur alone was applied and this was only slightly better than that produced by sulfur and calcium carbonate. Where sulfuric acid was added the growth of the barley was stunted, but the crop headed out and yielded an amount of grain slightly less than in those tanks receiving sulfur and calcium carbonate.

Field Experiments.—Five plots (21 to 25), each 40 by 135 feet, were staked out on one of the worst portions of the Kearney Vineyard Experimental Tract near Fresno, California, on May 10, 1923. The plots were given the following treatments: plot 21, 3000 pounds per

acre of sulfur and 4080 pounds of gypsum; plot 22, 3000 pounds per acre of sulfur and 3000 pounds of $CaCO_3$; plot 23, untreated; plots 24 and 25, 3000 pounds per acre of sulfur. Plot 25 was thoroughly leached with water by heavy flooding before the sulfur was applied, while the other plots were not flooded until several months after the treatments were applied. The materials were applied and plowed under on June 2, 1923. Before the experiments were begun thirteen samples were drawn from each plot to the following depths: 0–6 inches, 6–12 inches, 12–24 inches, 24–36 inches, and 36–48 inches. The samples were taken at 10-foot intervals along the center line of the plots, and later samples were drawn at places 6 inches distant from those of the original samples. A second set of samples was drawn on December 15, 1924, and a third on March 24, 1925, just after the plots had been thoroughly leached. Analyses were made on 1–5 water extracts of these samples.

The extreme variability of alkali soils greatly complicates the determination of the chemical changes occurring in a field experiment under any treatment. This has proved to be the case in these experiments. The brief period employed in these experiments is also a factor affecting the conclusions. The data obtained for the soluble carbonate and sulfate in the first foot, presented in tables 15, 16, 17, 18, and 19, indicate that a considerable amount of the alkalinity had been neutralized by each of the treatments.

TABLE 15

Composition of Plot 21, Treated with Sulfur and Gypsum May 15, 1923

Parts per million

Sample	May 1923		Dec. 1924		Mar. 1925	
	CO_3	SO_4	CO_3	SO_4	CO_3	SO_4
1	0	305	0	126	0	68
2	180	528	69	468	0	110
3	270	530	135	62	180	21
4	285	573	0	1370	162	51
5	186	788	90	624	30	98
6	210	500	0	3480	87	200
7	186	466	0	600	0	336
8	342	492	180	378	72	80
9	444	760	220	758	171	114
10	609	713	0	518	150	47
11	540	620	27	414	156	132
12	429	524	120	330	199	90
13	558	791	39	346	0	100

TABLE 16

COMPOSITION OF PLOT 22, TREATED WITH SULFUR AND $CaCO_3$ MAY 15, 1923

Parts per million

Sample	May 1923		Dec. 1924		Mar. 1925	
	CO_3	SO_4	CO_3	SO_4	CO_3	SO_4
1	156	41	109	318	78	69
2	204	151	259	236	171	67
3	138	202	222	580	144	48
4	210	690	210	192	195	74
5	180	654	168	546	141	96
6	189	460	0	418	0	156
7	174	189	195	190	153	106
8	231	781	150	394	150	71
9	390	534	135	748	219	156
10	489	736	231	222	114	150
11	402	883	180	332	174	466
12	438	885	231	496	264	586
13	531	848	135	524	0	532

TABLE 17

COMPOSITION OF UNTREATED PLOT 23

Parts per million

Sample	May 1923		Dec. 1924		Mar. 1925	
	CO_3	SO_4	CO_3	SO_4	CO_3	SO_4
1	210	171	150	176	24	30
2	180	716	330	392	249	16
3	120	431	240	534	354	49
4	300	603	330	380	300	30
5	180	653	270	358	330	20
6	130	655	90	624	171	59
7	141	86	150	456	216	44
8	150	1317	135	654	306	122
9	405	655	135	1014	390	292
10	360	602	240	540	366	41
11	270	696	345	384	429	116
12	420	790	375	734	330	38
13	390	524	285	114	240	33

TABLE 18

COMPOSITION OF PLOT 24, TREATED WITH SULFUR MAY 15, 1923

Parts per million

Sample	May 1923		Dec. 1924		Mar. 1925	
	CO_3	SO_4	CO_3	SO_4	CO_3	SO_4
1	330	328	24	578	30	136
2	200	347	0	834	138	126
3	390	461	156	392	216	130
4	261	379	30	660	288	276
5	210	108	0	592	0	246
6	240	107	63	1044	0	126
7	290	330	150	138	126	92
8	291	264	72	1040	156	79
9	510	2173	240	1134	240	302
10	354	294	210	2243	174	412
11	216	716	54	1354	0	272
12	150	633	165	342	120	130
13	171	464	74	624	24	130

TABLE 19

COMPOSITION OF PLOT 25, TREATED WITH SULFUR MAY 15, 1923, AFTER FIRST LEACHING THE SOIL

Parts per million

Sample	May 1923		Dec. 1924		Mar. 1925	
	CO_3	SO_4	CO_3	SO_4	CO_3	SO_4
1	330	313	0	1228	30	108
2	150	72	165	268	168	78
3	300	255	300	262	264	184
4	270	170	180	618	285	286
5	230	174	225	1332	270	116
6	180	95	195	300	465	523
7	300	577	21	646	126	64
8	201	106	30	340	159	42
9	702	1014	120	1022	54	67
10	465	306	75	840	234	56
11	360	514	114	482	132	42
12	270	994	24	704	180	61
13	189	309	66	244	30	86

The first indication of effect from the treatments was shown by the rate at which the soil absorbed water upon flooding. All of the treated plots had become reasonably permeable to water when leached. The dikes one foot high around each plot were twice filled with water, all of which was absorbed within 48 hours in the case of the treated plots. The check plot, No. 23, on the other hand, remained quite impervious; much of the water stood on the surface at the end of one week and it was finally necessary to tap off the pools of water by surface drains.

Hubam clover was planted on all the plots in April, 1925. The crop response was just as striking as was the physical change in the soil, and the growth obtained shows that the treatments have more greatly affected the soil than is indicated by the analysis. By October, 1925, the Hubam clover had produced an excellent growth on all of the treated plots, whereas it was an entire failure on the check plot.

The difficulty of interpreting the chemical analyses of these samples accords well with the ideas presented earlier in this paper. It is evident from the equilibrium studies presented above that the neutralization of a large part of the alkaline compounds of a soil may be effected without this result being shown by a determination of soluble carbonate. The determination of the extent of sulfur oxidation is also complicated by the large amounts of sulfates already present in the soil, which tend to move by capillarity as a result of seasonal climatic changes.

These difficulties may be overcome, however, after the lapse of time, as is shown by the results obtained from another experiment in the same field where sulfur was applied at the rate of 3500 pounds per acre on May 24, 1921. This experiment is being conducted by the Chemistry Department of the Citrus Experiment Station, and the results have been made available to the writer. The method of sampling the soil was similar to that previously mentioned. The analyses of the original samples were made by Mr. S. M. Brown and are presented for the first and fourth-foot depths only (table 20).

TABLE 20

EFFECT OF SULFUR ON FRESNO ALKALI SOIL

Sample	First foot								Fourth foot							
	Before treatment				2 years after treatment				Before treatment				2 years after treatment			
	CO_3	SO_4	Ca	pH	CO_3	SO_4	Ca	pH	CO_3	SO_4	Ca	pH	CO_3	SO_4	Ca	pH
1	195	509	0	10	0	279	77	6.8	45	160	0	9.1	70	430	18	8.3
3	253	23	0	10	0	1955	546	6.9	45	44	0	9.2	108	554	0	8.4
5	375	216	0	10	0	469	133	7.0	150	54	0	9.6	168	649	0	8.4
7	200	45	0	10	0	215	78	6.9	150	44	0	9.6	0	209	60	8.2
9	285	15	0	10	0	514	175	6.9	270	95	0	9.6	18	232	0	8.2
11	345	370	0	10	30	669	79	8.4	105	46	0	9.6	75	385	25	8.5
13	300	417	0	10	0	2024	311	7.2	30	40	0	9.0	78	584	80	8.4
15	345	169	0	10	21	1477	193	8.4	30	44	0	9.1	0	198	45	8.2
17	255	242	0	10	30	1676	210	8.4	105	39	0	9.6	150	171	21	8.4
19	375	618	0	10	40	421	62	8.3	210	73	0	9.6	86	406	0	8.4
21	435	381	0	10	10	904	117	8.2	30	62	0	9.0	0	266	32	8.2
23	540	884	0	10	0	592	133	7.0	465	72	0	9.6	330	192	9	8.5
25	510	610	0	10	0	1978	348	7.1	90	56	0	9.0	174	593	7	8.6

It is evident that the oxidation of sulfur has affected the soil of this plot to a marked extent, especially in the first foot. The effect has also extended into the fourth foot to some extent, showing that it is possible to affect this soil to a considerable depth by the application of sulfur.

The crop records obtained from this plot show that after the lapse of four years' time the effect from the application of sulfur was very striking. Although the effect was slow in manifesting itself, owing no doubt to the fact that the oxidation of sulfur is a biological process in which the time element is of considerable importance, the growth of alfalfa, four years after the sulfur was applied, was excellent.

SUMMARY

A brief review of the investigations on the replacement of bases in soils, the relation of base exchange to alkaline soils and the oxidation of sulfur, is presented in this paper.

Sulfur oxidation took place very readily in alkaline soils under laboratory, greenhouse, and field conditions, and was most rapid in sandy soils and in the presence of sodium carbonate. Carbonates and bicarbonates were decomposed and bicarbonates and sulfates formed during sulfur oxidation, but no stoichiometric relationship was found between these processes.

The fact that the oxidation of sulfur brings about a simultaneous decomposition of carbonate and bicarbonate was investigated by studying the equilibrium between dilute sulfuric acid and calcium sulfate, and alkaline soils. The results showed that upon adding dilute sulfuric acid the amount of soluble sodium and potassium increased and sodium carbonate decreased, with only slight changes in the concentration of silica. With the approach of complete neutralization of the sodium carbonate, the concentration of calcium and magnesium increased. By assuming an exchange of hydrogen ions, stoichiometric with the increase in soluble sodium, potassium, calcium, and magnesium, it was possible to quantitatively account for approximately all of the acid added. Hydrogen ions were found to function as a replacing agent to a greater extent than calcium, even though considerable amounts of calcium were made soluble.

The addition of dilute sulfuric acid effects a partial neutralization of carbonate to the bicarbonate stage, while calcium sulfate brings about a precipitation of carbonate in the form of calcium carbonate. Hence, equivalent for equivalent, sulfuric acid is a much more efficient neutralizing material than calcium sulfate. In the light of the data

obtained from sulfofication studies, on the one hand, and equilibrium studies, on the other, it is hypothecated that sulfur undergoes oxidation around the particles of calcium carbonate, forming calcium sulfate, and that the organisms concerned utilize more or less of the carbon dioxide thus formed as a source of carbon.

Results are presented of tank and field trials in which the greater part of the alkalinity of the soil has been neutralized by the addition of sulfur, and in the field trials very striking improvements have resulted in the crop yields. The presence of calcium carbonate is very desirable in the reclamation of an alkaline soil by means of sulfur.

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